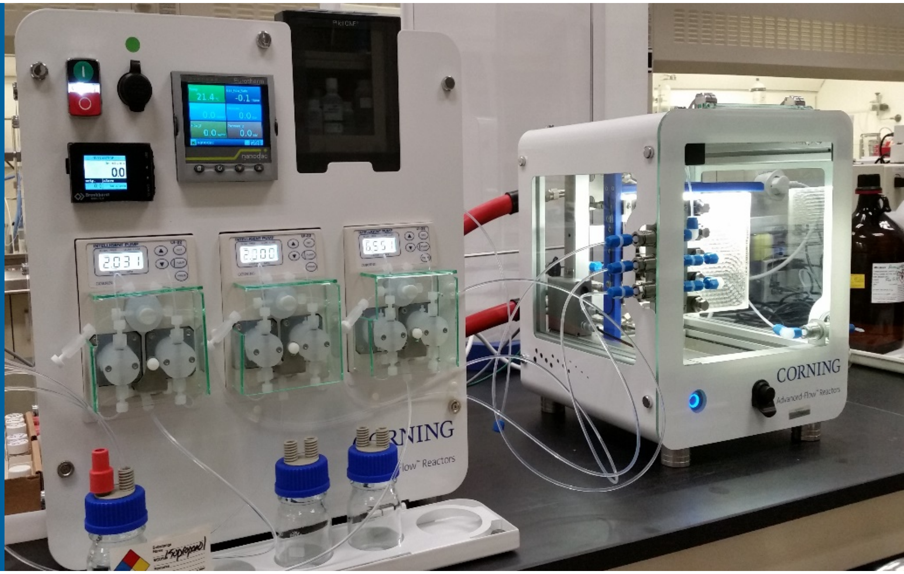
Process Development and Scale up of Critical Battery Materials – Continuous Flow Produced Materials



Trevor Dzwiniel **Kris Pupek (PI)**

Project ID: BAT 168

June 10-13, 2019, Arlington, VA

Overview

Timeline

- Project start date: Oct. 2010
- Project end date: Sept. 2020
- Percent complete: on going

Budget

- Total project funding:
  - $0.95M in FY18
  - $1.00M in FY19

Barriers

- New electrolytes are needed for advanced batteries.
- High cost of manufacturing advanced materials needs to be addressed.

Partners

- Scaling materials for:
  - Argonne's Applied R&D Group.
  - Zhang group (BAT374).
  - Argonne's FSP facility (BAT315).

- Supporting battery research for:
  - ADA Technologies
  - 24M Technologies
  - Army Research Laboratory
  - Naval Surface Warfare Center Carderock Division
  - Purdue University
  - Northern Illinois University
  - SilLion

Approach – FY 19 Milestones

- Flow Chemistry Development
  - Development of new continuous processes for fluorinated electrolyte solvents:
    - Trifluoroethyl methyl carbonate (FEMC) **complete**.
    - Bis(trifluoroethyl) carbonate (DFEC) development **complete**.
  - Continuous process for 3,3,3-trifluoropropylene carbonate (TFPC) is **ongoing**.
  - Synthesis of new Si-containing carbonate solvents in continuous flow is **ongoing**.
  - Process development of hexafluorobutylene carbonate (HFBC) is **ongoing**.

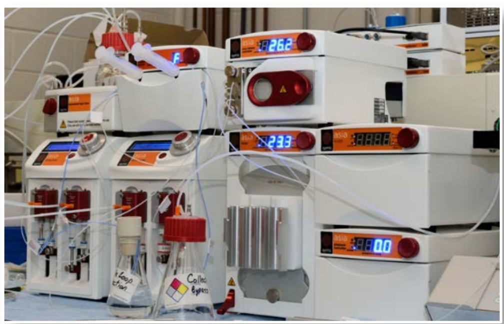
- Scale-up Programs:
  - Multi-kilo scale-up of new Al-LLZO precursors for FSP facility (BAT315) is **complete**.
  - Scale-up of methyl bis(fluorosulfonyl)imide (Me-FSI) is **complete**.
  - Development/ scale up of 3,3,3-trifluoropropylene carbonate (TFPC) is **complete**.

Objectives and Relevance

- The **objective** of this program is to provide a systematic research approach to:
  - Develop **cost-effective, scalable** processes for manufacturing of advance materials by more efficient use of feedstock and energy, improved safety and reduced environmental impact.
  - Evaluate **emerging synthesis technologies** for production of experimental materials.
  - Produce and provide **high quality and sufficient quantities** of these materials for industrial evaluation and in support of further research.
- The **relevance** of this program to the DOE Vehicle Technologies Program is:
  - The program is a key missing link between invention of new advanced battery materials, market evaluation of these materials and high-volume manufacturing.
  - Reducing the risk associated with the commercialization of new battery materials.
- This program provides large quantities of materials with consistent quality:
  - For industrial validation and prototyping in large format cells.
  - To allow battery community access to new materials and advance further research.

- Continuous flow chemistry is an emerging technology that promises to outperform traditional batch manufacturing processes.

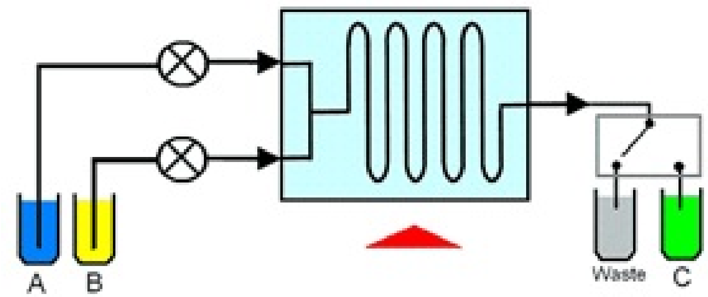
Approach and Strategy

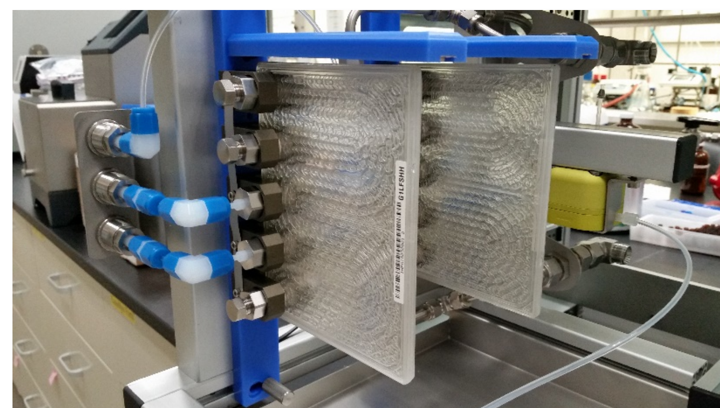


- Researchers in a basic science invent new materials, synthesize small amounts and evaluate electrochemical performance in small cell formats.
- MERF collects information about new materials, prioritizes them based on level of interest, validated performance and scale up feasibility. Discuss candidate materials with DOE for final approval.
- MERF evaluates new emerging manufacturing technologies, conducts process R&D, develops and validates optimal process parameters for production of new materials.
- Proof of concept in stages from 10g to 100g to Kg’s
  - Validate electrochemical performance.
  - Develop performance *vs.* purity and impurity profile relationship (material specification).
- Provide feedback to discovery scientists helping promote future research.
- MERF makes promising new materials available to assist basic researchers and to facilitate industrial evaluation.

Approach and Strategy

- In the quest for better, advanced electrolyte materials (solvents, salts, additives) scientists design, synthesize and evaluate more and more complex molecules.
- The complexity of the molecular structure is frequently translated into increased complexity and cost of the manufacturing processes.
- The program evaluates emerging synthesis techniques to address the cost issue.
- Continuous Flow Chemistry enables the synthesis of materials from discovery through process development and (possible) production scale in a cost effective manner.
- Continuous flow reactors can be used for rapid screening of reaction conditions to better understand fundamentals of process kinetics and thermodynamics.
- MERF demonstrates the feasibility of new continuous processes by scaling material manufacturing.

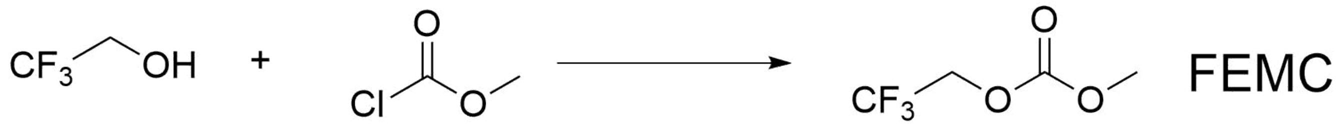




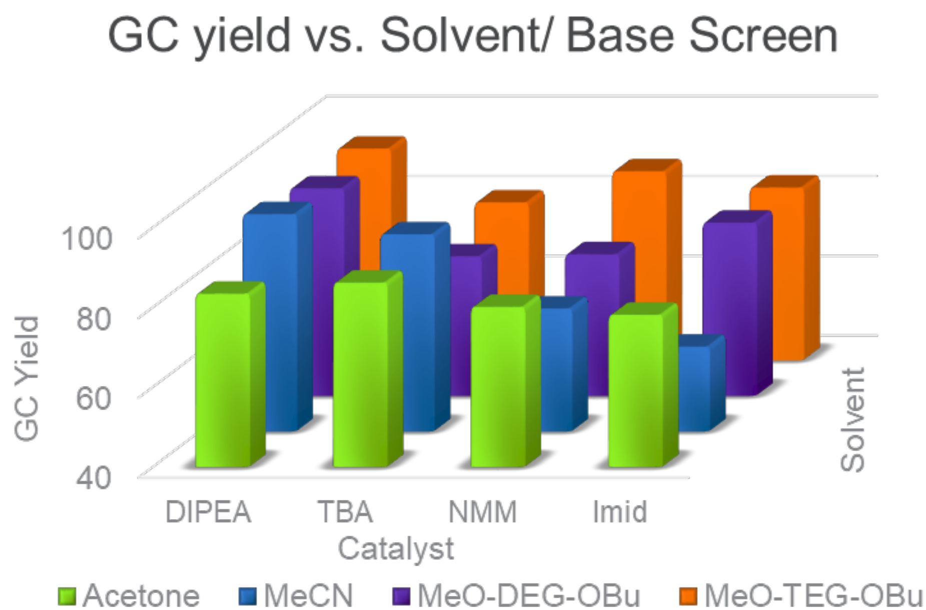
Technical Accomplishments

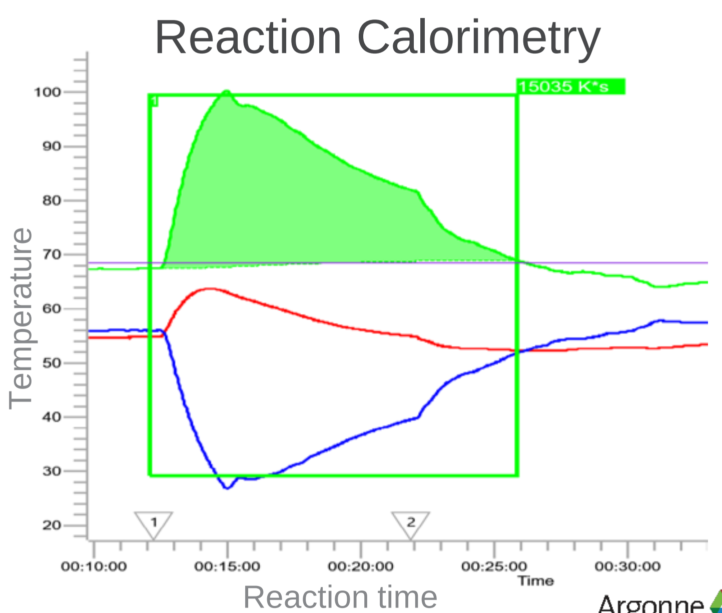
FEMC Redevelopment – Screening Conditions

- Batch process: K_2CO_3 slurry in acetone reacted with TFE and MeOC(O)Cl.
- Main issue to address for flow synthesis: suitable soluble conditions.



- 6x8 matrix of base and solvent was screened: few suitable candidates.
- Smaller 4x4 matrix analyzed by GC: selected EtN-*i*-Pr_2 and MeCN.
- Final issue: Exotherm control: ca. 120 kJ/mol; 560 W/L max heat flux.





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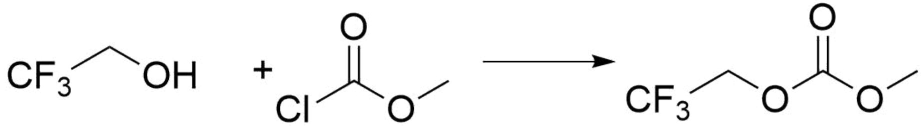
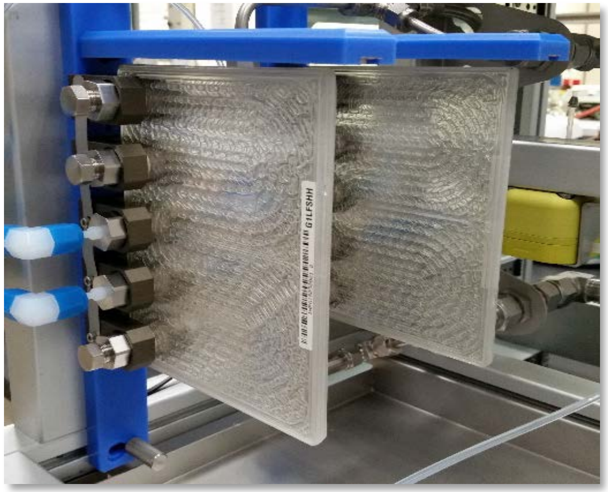
Technical Accomplishments

FEMC Redevelopment- Continuous Flow Mode Production

- Solution stability: TFE and in EtN-*i*-Pr_2 with MCF in MeCN.
- Second plate used for aqueous quench. Distillation gave pure FEMC.
- Prepared on 100's g scale over 8h.
- Preliminary cost evaluation: 16% increase in materials cost, 45% saving in time due to automation.



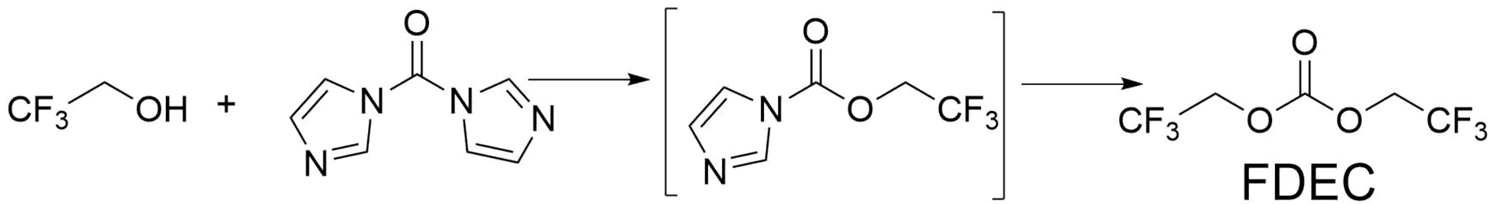


Conditions:
- TFE in EtN-*i*-Pr_2 (1.1 eq)
- MCF(1.1 eq) in MeCN (1.2 vol)
- Residence time 1 min, 55ºC.

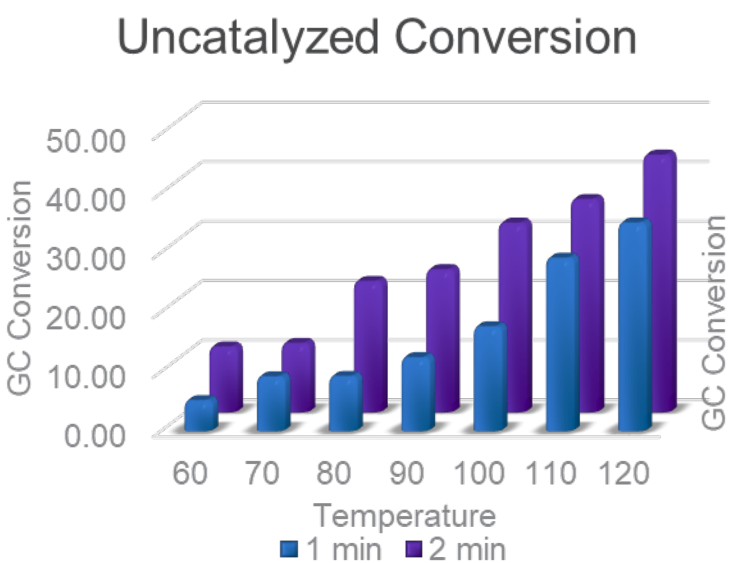
Technical Accomplishments

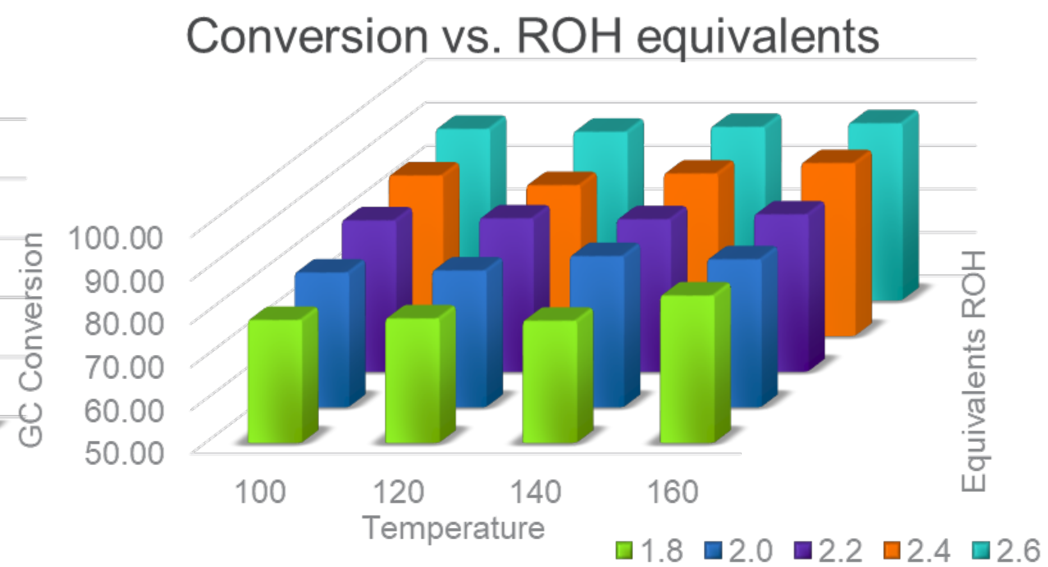
FDEC – Development for Continuous Flow Mode

- Original batch process uses a CDI slurry in MTBE reacting with TFE.
- Concerns: low CDI solubility, lack of suitable alternative, low conversion.



- Further research determined an amine catalyst was required for full conversion of intermediate to product, and dependent on reagent ratio.



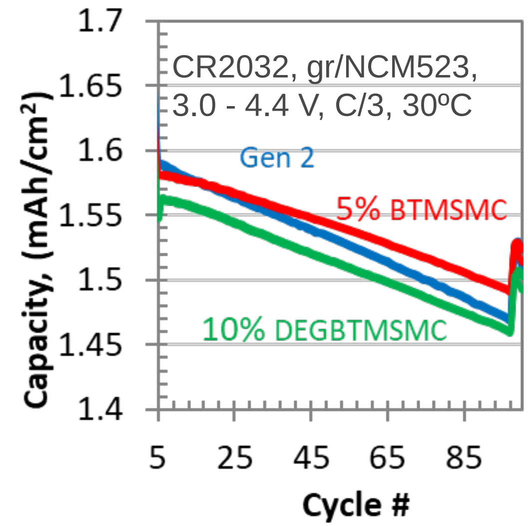


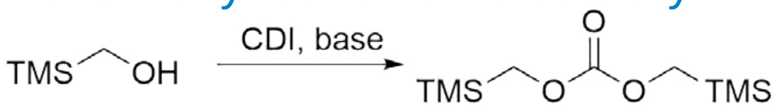
Conditions: 1M CDI in DMF, 2M TFE in DMF, 2.1 eq TFE, 5 mol% base, Residence time 4 min.

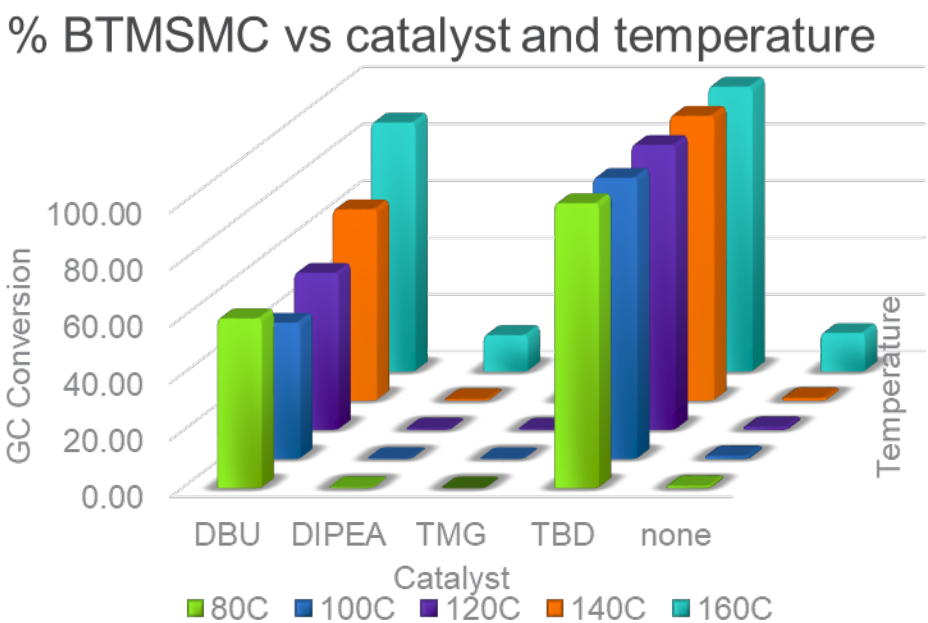
Technical Accomplishments

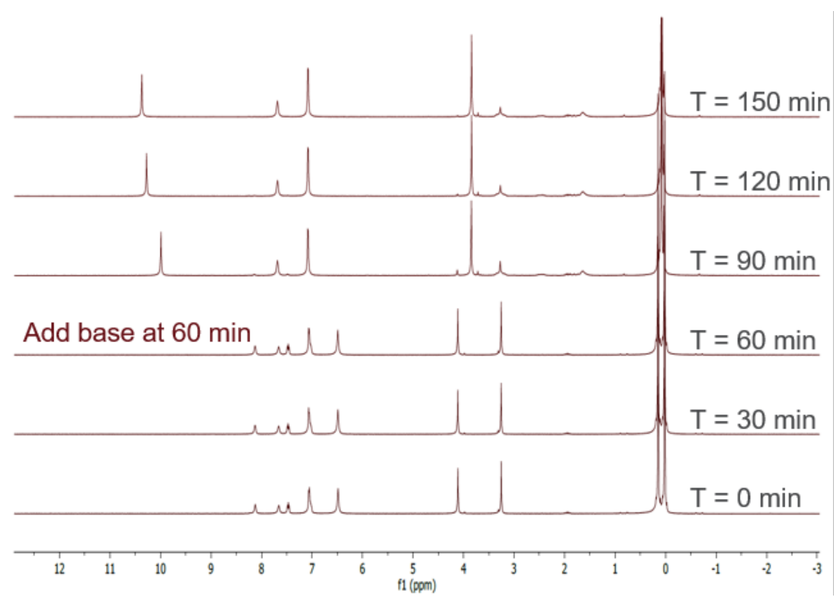
BTMSMC: Continuous Flow Mode

- Original process was not reliable: reaction time varied, incomplete, even with usual amine catalysts.
- Required specific bases, at least at 5 mol% in concentration. Confirmed by ^1H NMR.
- Simple aqueous workup and purification by distillation.
- Requirements of flow chemistry led to new discovery.



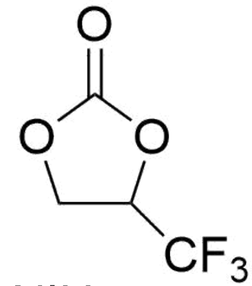




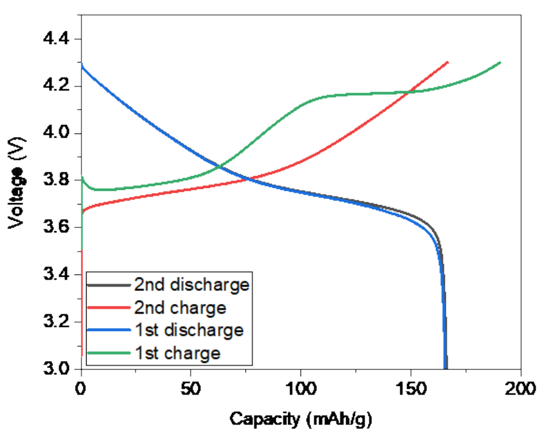


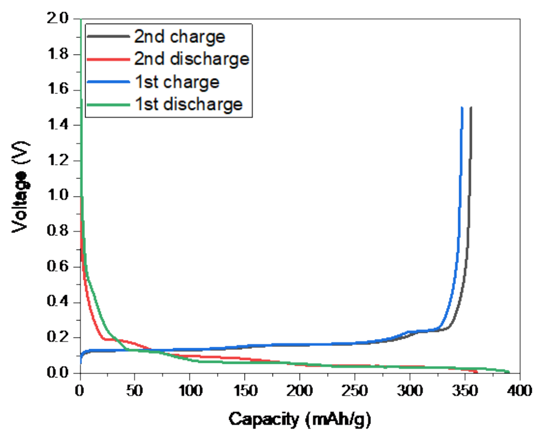
Technical Accomplishments

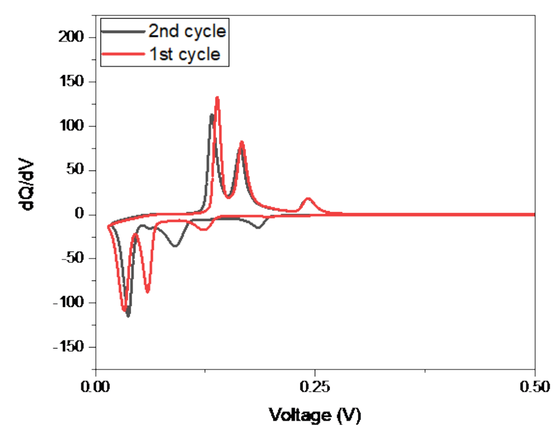
Trifluoropropylene Carbonate (TFPC) Usefulness



- Why TFPC?
  - Useful in-demand material for high voltage batteries.
    - Samples requested by SilLion, 24M, GM, ARL, PNNL, ANL, NIU.
    - Shows better temperature and voltage stability.
    - Less current leakage than EC at 4.9-5.2 V (Zhang *et.al*: *J. Electrochem. Soc.*, **162** (9) A1725-A1729 (2015).
    - Forms a stable SEI layer without EC (data courtesy J. Zhang, ANL).







NMC532/Li TFPC/TTE 5:1 1.0M $LiPF_6$; 3.0 – 4.3V, C/20 formation, C/3 cycling

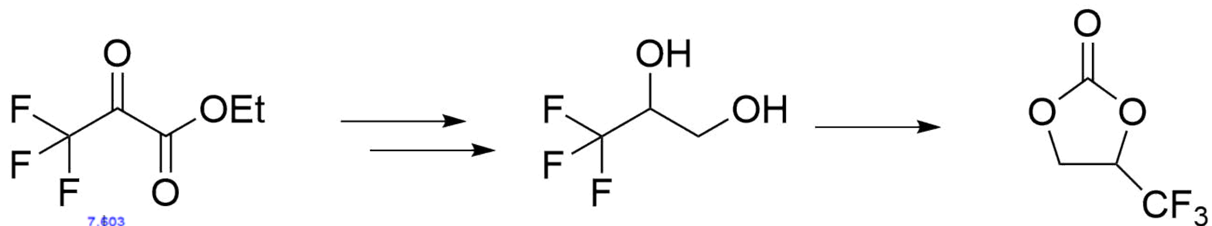
A-12 Gr/Li TFPC/TTE 5:1 1.0M $LiPF_6$; 0.01-1.5 V, C/10 formation, C/3 cycling

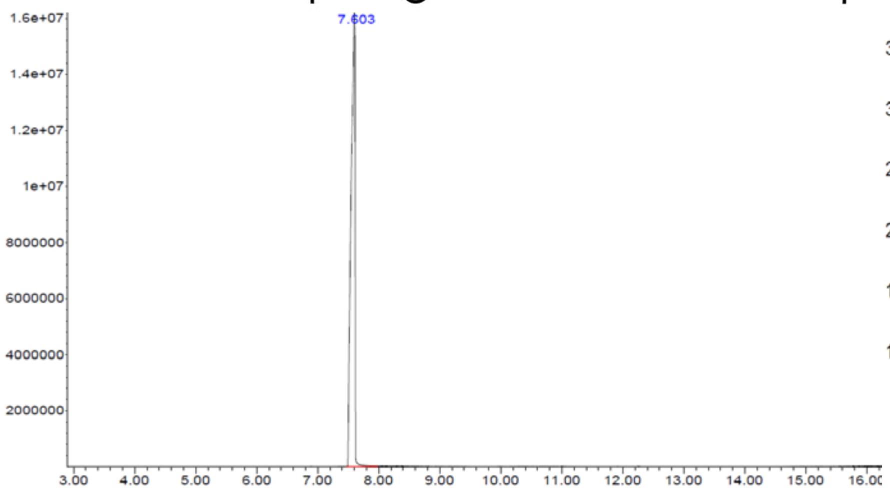
TTE = 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether

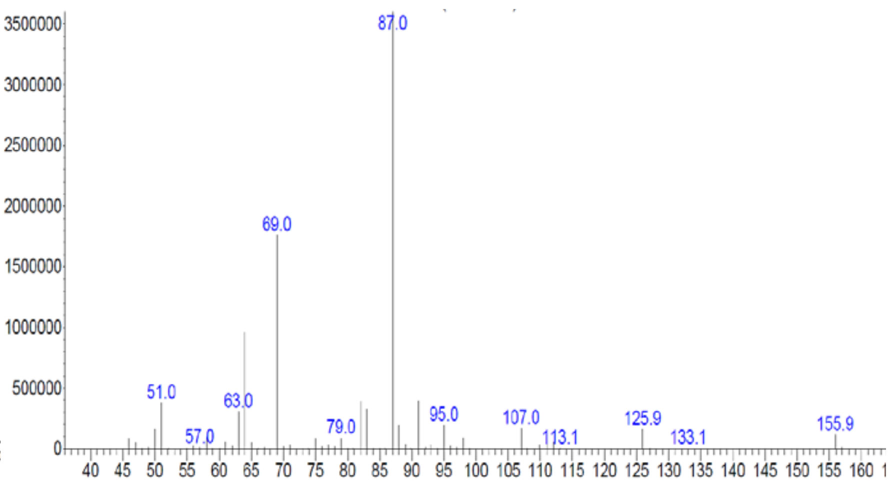
Technical Accomplishments

Improvement to the Batch Synthesis of TFPC

- MERF researched a novel, chlorine-free, safe and environmental friendly process to manufacture the material.
- MERF refined the batch process to achieve purity >99.5%.
  – Better yield from reaction optimization led to easier isolation.





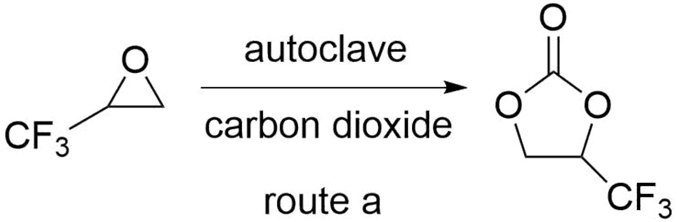


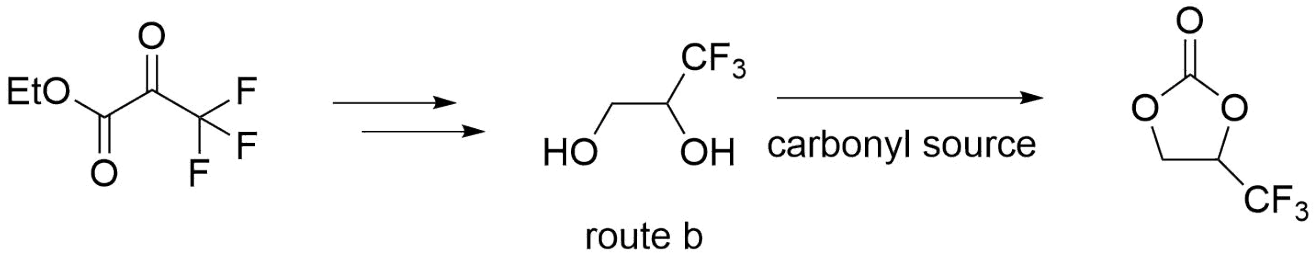
- *Can this be improved further?*

Technical Accomplishments

Improvement to Batch TFPC?

- Review two main synthesis options:
  - (a) epoxide: high pressure autoclave.
  - (b) diol: highly toxic carbonyl source e.g. phosgene, triphosgene.
- We have developed route (b), with less hazardous reagents (US 20180079708).
- Can this material be made continuously?





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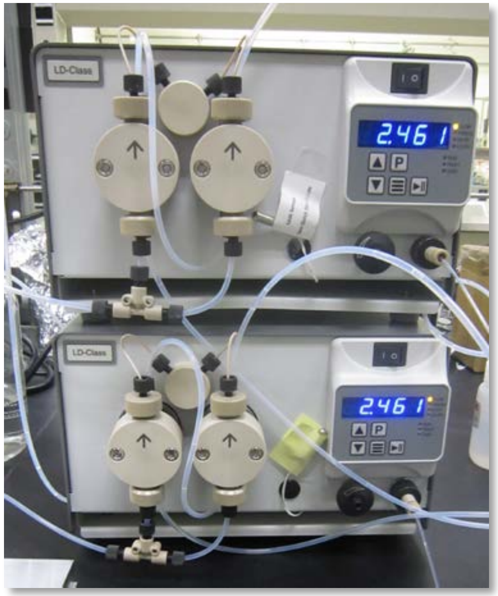
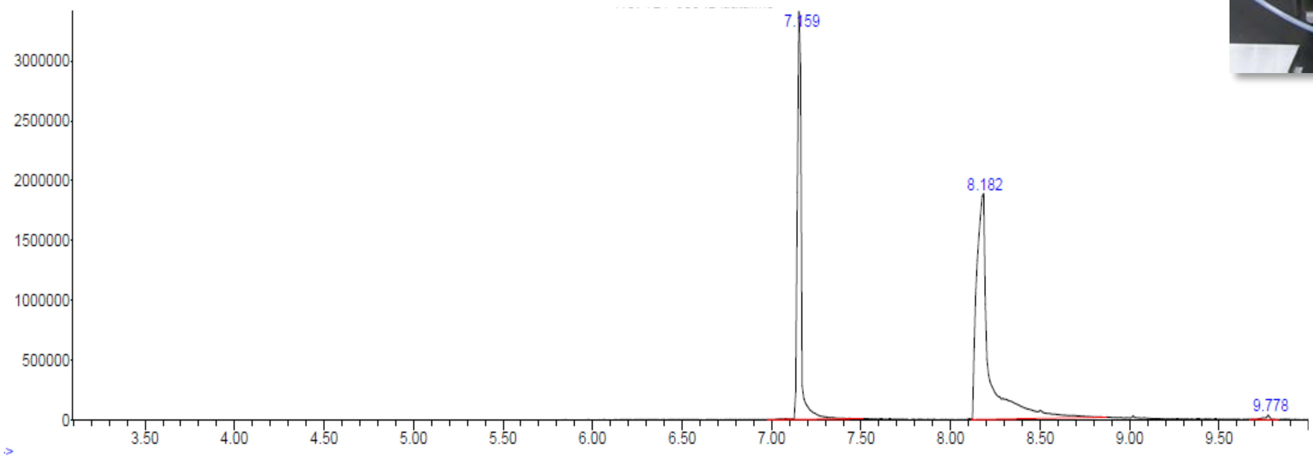
Technical Accomplishments

TFPC Semi-Batch Process

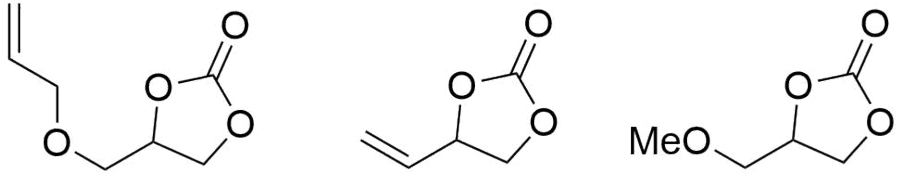
- Final step re-investigated using continuous flow chemistry. All conditions worked; milder than expected.
- Sample prepared simply using 2 HPLC pumps feeding a 4ml PTFE tube reactor. GC showed only product and byproduct: clean reaction and easy purification.
- Other diols showed similar enhanced reactivity.
  - Preliminary results indicate hexafluorobutanediol also reacts.





Conditions:
- 0.5M CDI in MeCN
- 0.5M diol in MeCN
- 50ºC, 1 minute

  - Also made are:



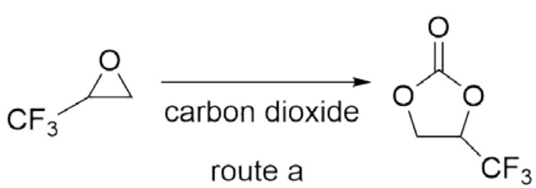
Technical Accomplishments

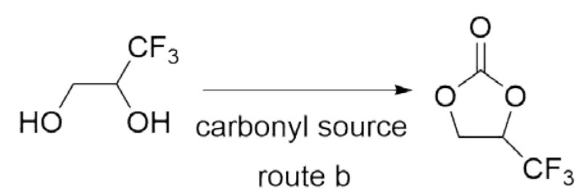
TFPC in a Completely Flow Process

- Both routes are batch processes, and are difficult to scale up (notably route a).
- However, route (a) has promise:
  - Fewer overall steps: less time.
  - All materials are commercial.
- Main drawback: requires autoclaves and long reaction times.
- Flow chemistry technology represents a new opportunity, but traditional chip reactors are not well-suited for gases.
- Corning flow reactor: safe high pressure continuous manufacturing using gases!

Traditional flow cell

Corning flow cell

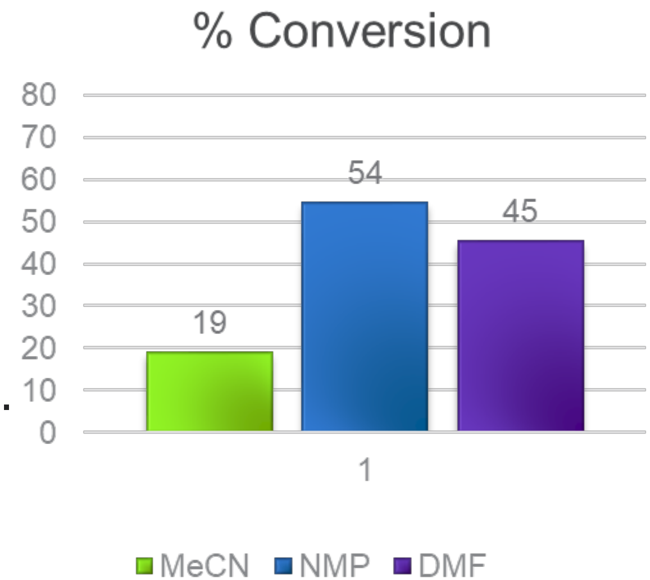


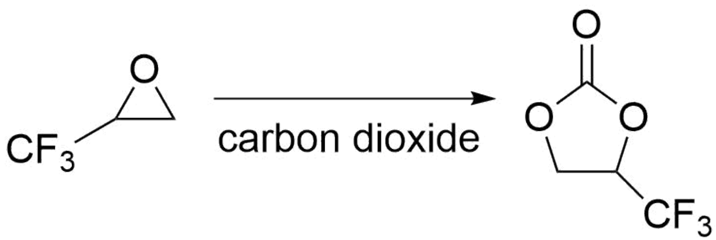


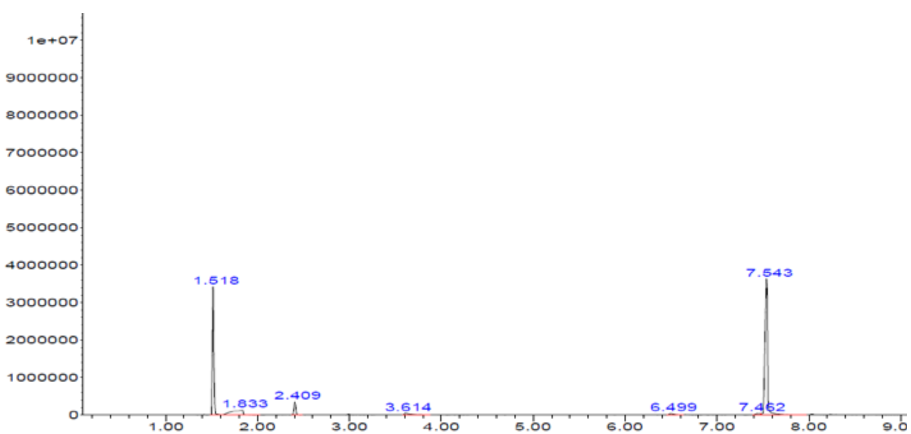
Technical Accomplishments

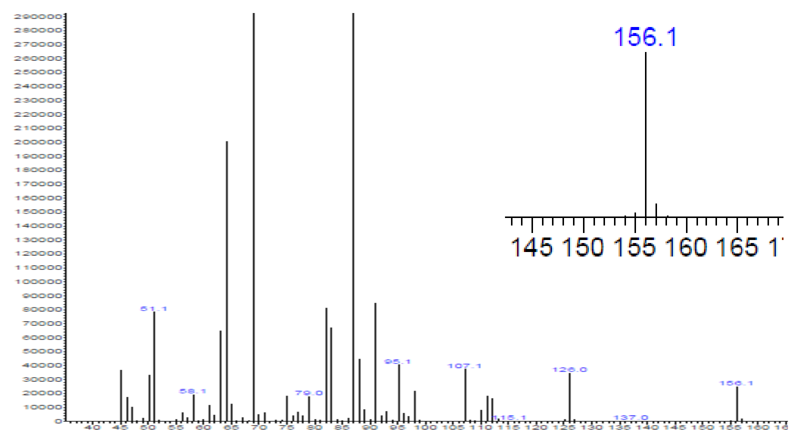
TFPC Flow Process

- GC/MS confirms that product (m/z 156) formed.
- Initial exploration shows a strong effect by both catalyst and solvent on conversion.
- Further development and optimization in progress.



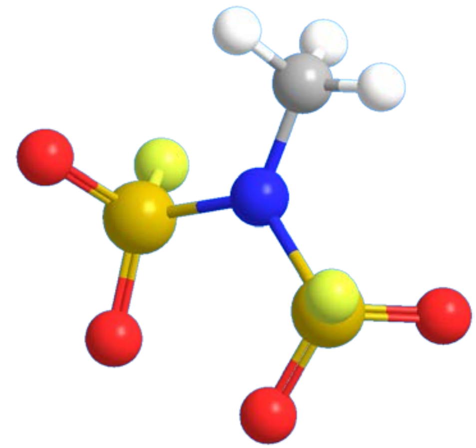




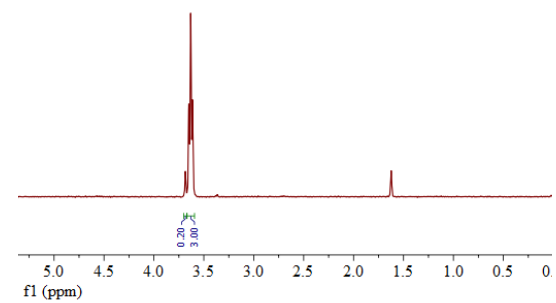


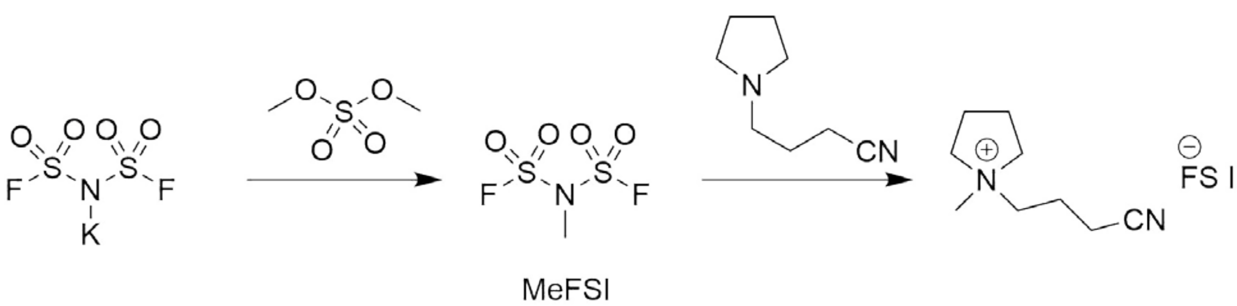
Technical Accomplishments

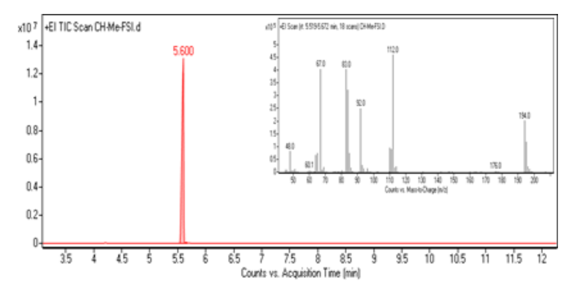
Other projects: Me-FSI



- Needed for salt-free synthesis of new Ionic Liquids (IL's) formulations.
  - Non-flammable electrolytes.
  - Improved viscosity and Li-ion conduction.
- One step synthesis: requires high purity materials.
- Scale-up safety concern: workup modified to diminish large heat release.
- Further IL studies in progress with Zhang group.



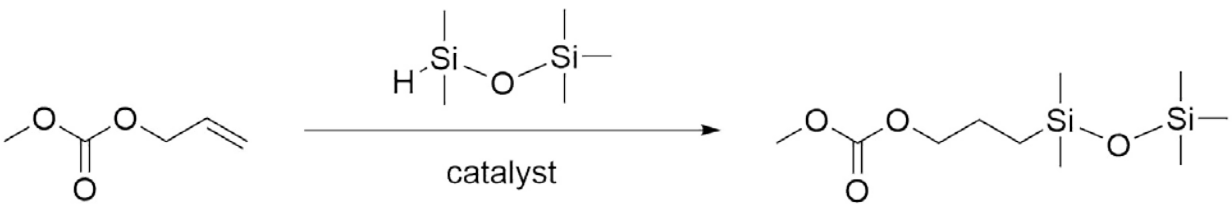




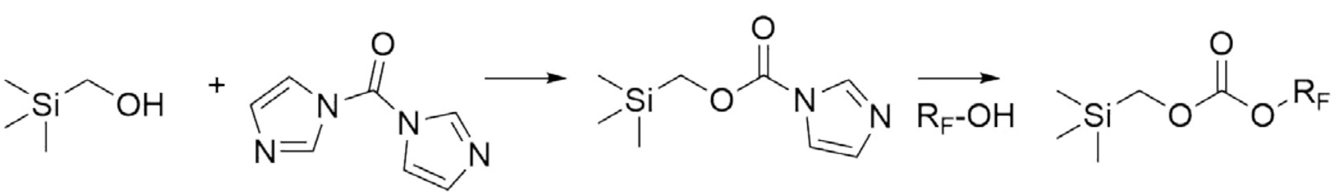
Technical Accomplishments

Si-containing Carbonate Solvents

- High voltage Li-ion battery still do not have optimal electrolyte solutions.
- Silicon-containing carbonates may be beneficial as either additives or solvents.
- Batch processes:



- Flow processes:
  - Preliminary work underway on synthesis of unsymmetric carbonates using flow technology.
  - Although the initial reaction is smooth, control over the addition of the second alcohol fragment is difficult.



Response To Previous Year Reviewer' Comments

- <u>Question 1</u>: Approach to performing the work
- Reviewer 3: The reviewer commented that our approach "does not begin to approach a pilot scale…for...industrial production". Our intent is to develop a scalable process and provide the technical and engineering baseline needed for this level of manufacturing, which is generally unavailable from literature reports of bench-scale processes. We do not physically manufacture material at this scale, but will collaborate with industrial partners with this capability and interest.
- <u>Question 2</u>: Technical accomplishments and progress
- Reviewer 1: The reviewer commented that it would have been helpful to provide an update on how much material and how many samples have been delivered. We maintain a database tracking this information, but do not typically present this data at AMR. As of April 2019, over 200 samples and well over 15kg of electrolyte materials have been distributed.
- <u>Question 4</u>: Proposed Future Research.
- Reviewer 2: The reviewer suggested that the number of materials to be scaled be reduced to allow complementary efforts (cost analysis, scale-up innovation and sample verification). We have narrowed our number of targets to focus more on innovative flow chemistry processes, and we plan to run additional verification tests that have previously run by the material inventor.
- Question 5: Relevance.
- Reviewer 3: This reviewer commented that adding industrial collaborators/feedback would strengthen this project. We agree. We are actively looking for additional industrial partners. Due to the proprietary nature of the information, industry is not always willing to provide feedback.

Remaining Challenges And Barriers

- New advanced battery chemistries call for new and/or reformulated materials.
- New electrolyte materials are being continuously invented and tested in laboratories but only limited quantities are available to evaluate basic properties and performance.
- There is a strong demand from the research community for high quality, uniform experimental materials.
- Large quantities of these high quality experimental new materials are needed for industrial validation and prototyping.
- Industry is typically unable to accurately model the cost of production based on bench scale procedures.
- New materials also need to be evaluated for performance to be successfully introduced to the market.
- Emerging manufacturing technologies need to be evaluated to address production costs of battery materials.
- MERF has the capability to evaluate, manufacture, and distribute large quantities of new materials to assist the battery community.

Collaborations

Process R&D and material scale up:

- Argonne National Laboratory
  - High voltage solvents (John Zhang)
- Precursors for Al-LLZO (FSP Facility)

- **Material samples provided for further research:**
  - Army Research Lab
  - 24M Technologies
  - Purdue University
  - Lawrence Berkeley National Lab
  - Pacific Northwest National Lab
  - ADA Technologies, Inc.
  - General Motors
  - SilLion
  - Northern Illinois University
  - Naval Surface Warfare Center Carderock Division

- **Other Collaboration:**
  - Advano

Activities For Next Fiscal Year

- Process R&D and Scale Up - Target 2-3 new materials.
  - Evaluate and select the best synthesis technique and route for each new material.
  - Develop scalable process, analytical methods and quality control procedures.
  - Validate the manufacturing process for material quality consistency.
  - Characterize the impurity profile.
  - Supply material samples to the research community and industry for their evaluation.
- Investigate chemical purity vs. electrochemical performance for new materials.
- Continue evaluate new technology platforms with a focus on Green Chemistry and economy of the process.
- Continuous flow chemistry will continue to be a major focus due to:
  - Fast mass and heat transfer; accurate control of reaction condition.
  - Allow rapid optimization of reaction parameters.
  - Low usage of reagents in the optimization process.
  - Dramatically increased process safety is realized.
- Program is open to suggestions for scaling up newly invented, promising battery materials.

Summary

- Continuous flow reactor technology was developed and evaluated.
- This emerging manufacturing technology platform permits expedited process R&D and rapid “proof of concept” materials production.
- Flow reactor systems reduce time and cost associated with process R&D.
- Efficient continuous methods for manufacturing several advanced electrolyte materials (FEMC, BTMSMC, TFPC) were developed.
- Scope, limitations and benefits of producing other advanced materials in continuous flow process are investigated.
- Precursors for FSP production of Al-LLZO were scaled up to multi-kilo levels.

- **Sample of all materials produced at MERF are available to support basic research and for industrial validation.**

Acknowledgements And Contributors

- Continuous support from Steven Boyd, David Howell and Peter Faguy of the U.S. Department of Energy's Office of Vehicle Technologies is gratefully acknowledged.

- Argonne National Laboratory
- MERF Critical Battery Materials Team
  - Kris Pupek
  - Trevor Dzwiniel
  - Chia-Wei Hsu
  - Alex Ross
  - Gerald Jeka
  - Andrew Turczynski

Support and Collaboration

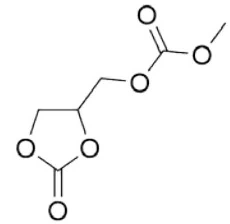
- Joseph Libera
- Daniel Abraham
- Christopher Johnson
- Andrew Jansen
- John Zhang
- Bryant Polzin
- Steven Trask
- Allison Dunlop
- Wenquan Lu
- Qian Liu

For samples and further information: Kris Pupek kpupek@anl.gov, www.anl.gov/merf

Technical Back-up Slides

Technical Back-up Slides: Feedback

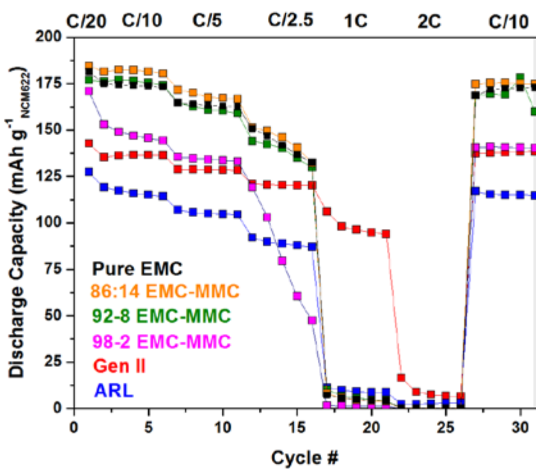
Glycidyl Methyl Dicarbonate (MGC or MMC)



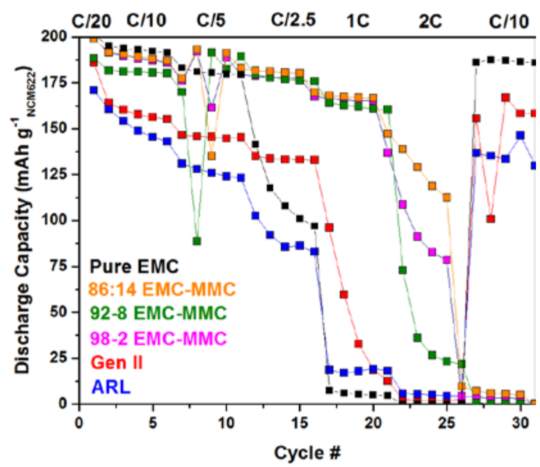
- MERF regularly requests feedback regarding material performance. Barriers such as proprietary data and feedback time exist.
- MERF developed scalable proprietary process for high purity material (>99.9%).
- Send to ARL in late 2016. Data courtesy Marshall Schroeder (ARL) received April 2019.

Capacity Retention (Voltage Window)

NCM622/Li Half Cell (3.5-4.4V)
C=182mAh/g_{NCM622}



NCM622/Li Half Cell (3.5-4.6V)
C=220mAh/g_{NCM622}



- Results show MMC supports capacity retention except at high rates.
- Full cell results suggest detrimental behavior at graphite/electrolyte interface.

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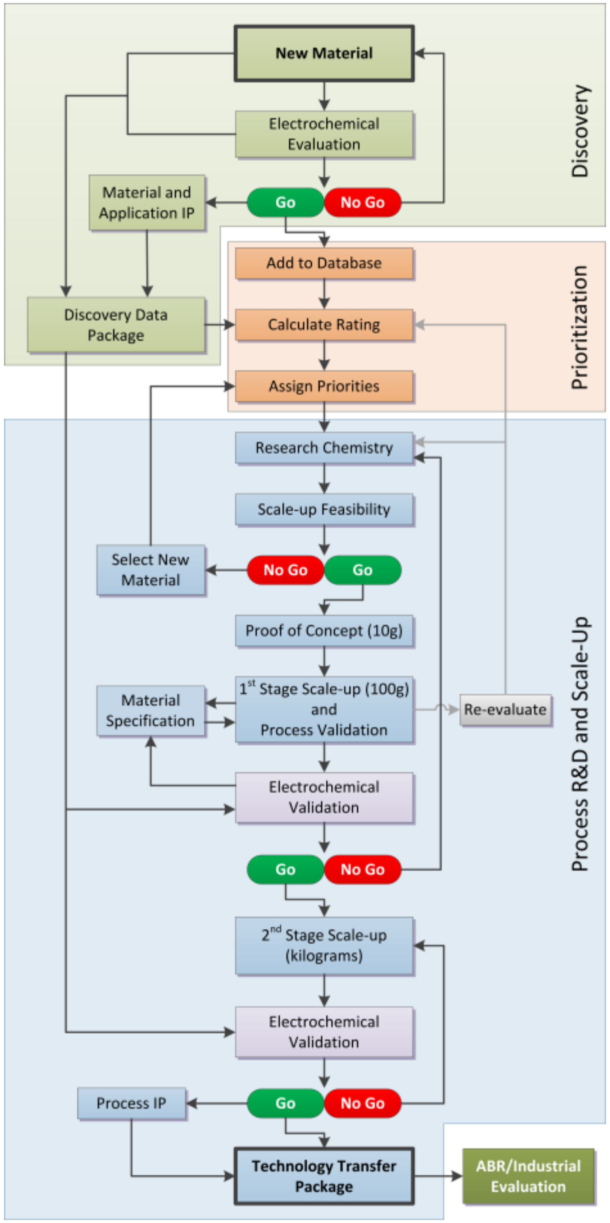
Technical Back-up Slides: Approach Flowchart



Work with discovery chemists to learn about promising new materials.

Collaborate on special requests for custom materials not commercially available.

Maintain a database of potential materials to scale.

Prioritize materials based on systematic approach including level of interest, validated performance and feasibility.

Discuss candidate materials with DOE for final approval.

Conduct process R&D and take materials through the stages of scale-up.

Develop material specifications that meets electrochemical performance at the lowest cost.

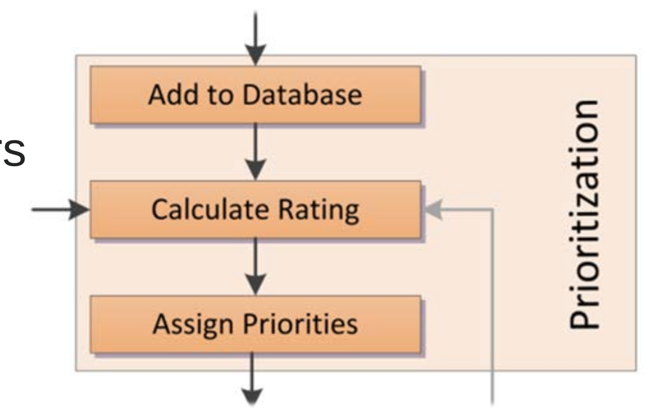
Make materials available for industrial evaluation and to the R&D community for basic research.

Provide feedback to discovery chemists, helping guide future research.

Technical Back-up Slides: Candidate Materials

Electrolyte Material	Chemical formula/ full name	Date added to spreadsheet	Organization	IP or patent #	Main Reference	Redox Potential (vs Li^+/Li)	Solubility in Electrolyte (1.2M LiPF6 EC/EMC (3/7 V/V))	Diffusion coefficent ($cm^2\ S^{-1}$)	100% Overcharge Cycling Stability	Side Effect Prior Overcharge	Chemical Stability	Ionic Conductivity (in Electrolyte System)	Viscosity (in Electrolyte System)	Applicable Chemistries	Electrochemical Evaluation (Y/N) (attached if Y)	Industrial/Commercial Interest (1-10, best 10)	Material Performance (1-10, best 10)	Intellectual property clear (Y/N)	Scale previously achieved/ commercial (#g or unknown)	Number of Validations/ Syntheses (# or unknown)	Number of Synthetic Steps (# or unknown)	Product commercially available? (Y/N)	Cost (L/M/H)	Safety Hazard (L,M,H)	Raw Materials Readily Availability (Y/N)	OVERALL SCALE SCORE (best score 89)	Commercially available No/Yes (green/red)	Electrochemical Evaluation Yes/No (green/red)	Intellectual Property Clear (Y/N)	Raw Materials Available (Y/N) (green/red)
ANL-1NM2	$(CH_3)_3SiO(CH_2CH_2O)_3CH_3$	11/1/2010	Argonne National Laboratory	unknown	unknown	4.89	0.9	LiTFSI only	2.5	5	68	0.32	250	$LiMO_2$ (Co, Mn, Ni) $LiMn_2O_4$ $LiFePO_4$	Y	8	5	Y	50	2	1	N	L	L	Y	61	No	Yes	Yes	Yes
ARL-HFIPP	tri(hexafluoro-iso-propyl)phosphate (C3HF6O)3PO	12/10/2011	Army Research Laboratory	unknown	Cresce & Xu, JES 158 A337 (2011)	unknown	<10%		unknown		Highly Moisture sensitive			LMNO 4.6 V	Y	10	7	Y	500	5	1	N	L	M	Y	71	No	Yes	Yes	Yes
ARL-PFTBP	tris(perfluoro-tert-butyl)phosphate (C4F9O)3PO	1/12/2012	Army Research Laboratory	unknown	unpublished	unknown	~10%	unknown	unknown	unknown	Moisture sensitive	unknown	Unknown	Protects cathode surface at high potentials	unknown	10	7	unknown	5	2	1	N	M	M	Y	57	No	unknown	unknown	Yes
ANL-RS2	2,5-di-tert-butyl-1,4-di-(2-methoxyethoxy)benzene (DBDMB)	11/1/2010	Argonne National Laboratory	ANL-IN-09-082 unpublished	US 2011/0294003	4.00V	0.5M	in progress	200 cycles for $Li/LiFePO_4$ 200 cycles for $Li_4Ti_5O_{12}/LiFePO_4$ 200 cycles for $MCMB/LiFePO_4$	Stable	Stable in air	Excellent	Medium	$LiFePO_4$	Y	9	8	Y	1	5	2	N	L	L	Y	68	No	Yes	Yes	Yes
ANL-RS21	Confidential - Patent Pending	1/11/2012	Argonne National Laboratory	unknown	unknown	4V	> 0.4M	unknown	150 cycles	stable	stable in the air	excellent	Low	LiFePO4	unknown	8	8	Unknown	5	3	1	N	L	M	Y	62	No	unknown	unknown	Yes
FRION	Confidential - Patent Pending	2/1/2013	Case Western University	unknown	unknown	unknown	unknown	unknown	unknown	unknown	Moisture sensitive	Excellent	unknown	unknown	unknown	unknown	unknown	unknown	2	5	unknown	N	unknown	unknown	Y	53	No	unknown	unknown	Yes

- Establish candidate materials by interaction with battery researchers in:
  - ABR/BATT funded programs to add novel materials.
  - Organizations looking to have known materials scaled.
  - DOE programs who want to use novel materials in their own research programs.
- Add materials by closely monitoring the trends in the battery research community.
  - e.g., high voltage materials.
- Prioritize materials – Ranking based on:
  - Level of interest and guidance from stakeholders from ACCESS advisory board.
  - Material performance and impact.
  - Prioritization criteria.
  - DOE guidance.



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